Polymer Bulletin 25, 161–168 (1991)

Polymer Bulletin

# Stereoregular polymerization of polyisobutylene macromonomer having methacryloyl function

**Tatsuki Kitayama, Shigeki Kishiro, and Koichi Hatada***

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

## Summary

The polyisobutylene (PIB) macromonomer having methacryloyl function was prepared from a hydroxy-terminated PIB, $\alpha$-phenyl-$\omega$-(2-hydroxy-1-methylethyl)-poly(1,1-dimethylethylene) and methacryloyl chloride in the presence of triethylamine. The macromonomer was polymerized by various anionic initiators to form stereoregular polymacromonomers. The polymerization of the macromonomer with t-$C_4H_9MgBr$ and n-$C_4H_9Li$ in toluene gave isotactic polymacromonomers. On the other hand, syndiotactic-rich polymacromonomers were obtained in the polymerizations with 1,1-diphenylhexyllithium in tetrahydrofuran and with t-$C_4H_9Li/(C_2H_5)_3Al$ in toluene.

## Introduction

Many investigations have been made on the preparation and polymerization of macromonomer aiming at the structural control of graft copolymer and comb-like polymer. The stereostructure of polymacromonomers would affect their properties greatly, but little attention has been paid on the stereoregularity of the polymer and copolymer of macromonomers[1-4]. We have reported the preparation of isotactic and syndiotactic poly(methyl methacrylate) (PMMA) macromonomers with styrene end group, which give comb-like polymers or graft copolymers with stereoregular branches. In the radical polymerization of these macromonomers, the isotactic macromonomer exhibited higher reactivity than the syndiotactic one[1-3].

In this paper, we will report stereoregular polymerization of a macromonomer, leading to the control of main chain stereoregularity of branched polymers. The macromonomer employed in the present work is a polyisobutylene (PIB) macromonomer having methacryloyl moiety as a polymerizable function. The methacrylate unit was selected by reason that stereoregular polymerization of methacrylate has been well surveyed[5]. Anionic polymerization of polystyrene macromonomers having methacryloyl function was carried out by Masson et al.[6] and Asami et al.[7]. However, the main objective of their works was to control the molecular weight and its distribution (MWD) of the polymacromonomers, and the main chain tacticity was not examined.

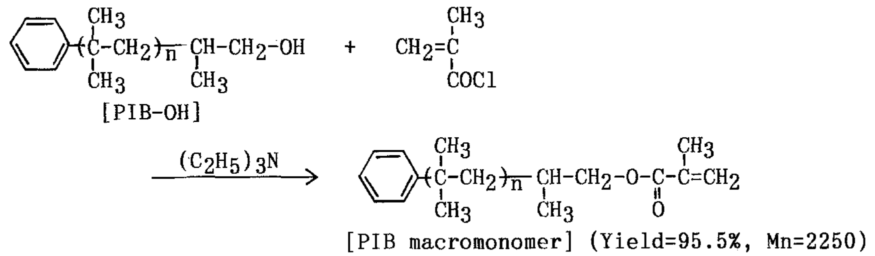
---

*To whom offprint requests should be sent

## Experimental

### *Preparation and anionic polymerization of PIB macromonomer*

The PIB macromonomer having methacryloyl function was prepared from a hydroxy terminated PIB (PIB-OH) (Mn=1990, Mw/Mn=1.15, DP=33.1) and methacryloyl chloride in the presence of triethylamine in a mixture of $CH_2Cl_2$ and $CHCl_3$ (9:1) at room temperature according to the procedure by Kennedy et al.[8] (eq. 1). The macromonomer was purified by precipitation from hexane to acetone. The hydroxy terminated PIB was obtained from Akron Cationic Development Corporation.



(1)

The polymerization of the macromonomer was carried out under dry nitrogen in a sealed glass ampoule. The macromonomer was dissolved in benzene and the solution was dried over $CaH_2$. Just before the polymerization, $CaH_2$ was removed by filtration under dry nitrogen, and the macromonomer was recovered by freeze-drying. The polymerization was initiated by adding a solution of the macromonomer to an initiator solution. After a certain polymerization time the reaction mixture was quenched by adding 1N HCl solution in methanol. The polymacromonomer formed was isolated by repeated reprecipitation from toluene to methanol.

### *Measurement*

$^1H$ NMR spectra were recorded on a JNM GX-270 spectrometer(JEOL) at 270MHz and $^{13}C$ NMR spectra on a JMN GX-500 spectrometer at 125MHz. Number average molecular weights (Mn's) were measured on a Hitachi 117 vapor pressure osmometer (VPO) in toluene at 60.0°C. Gel permeation chromatography (GPC) was performed on a JASCO FLC-A10 chromatograph equipped with Shodex GPC columns A-80M and KF-802.5 using THF as an eluent. The chromatograms were calibrated against standard polystyrene samples.

## Results and Discussion

### *Preparation and characterization of PIB macromonomer*

As mentioned previously, PIB macromonomer was prepared from PIB-OH and methacryloyl chloride in the presence of triethylamine. The $^1H$ NMR spectra of the starting alcohol, PIB-OH, and the resulting PIB macromonomer are shown in Figure 1. The PIB-OH shows the signals of $-\underline{CH_2}-OH$ and phenyl protons at 3.4ppm and 7.0-7.5ppm, respectively (Figure 1b).

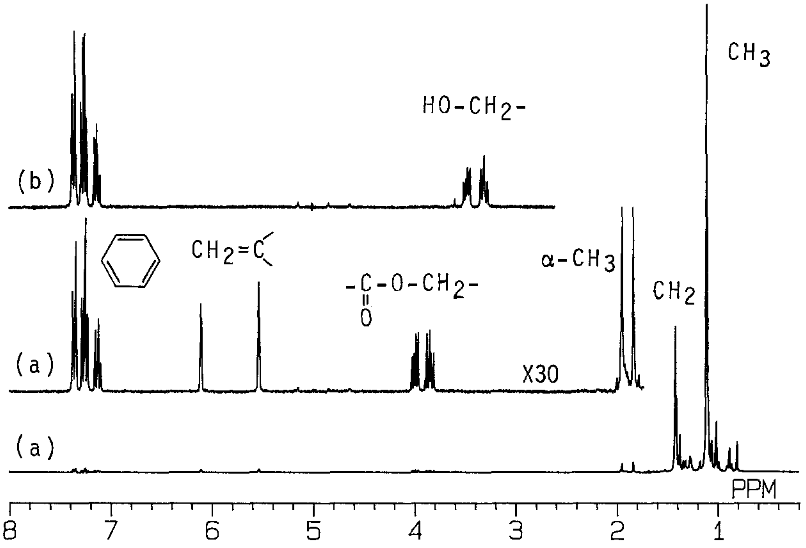


Figure 1 270MHz $^1$H NMR spectra of PIB macromonomer (a) and hydroxy-terminated PIB (b).

The functionality of hydroxy group of PIB-OH was determined from the intensity ratio of these two signals as 0.918. In the spectrum of the PIB macromonomer (Figure 1a), the signals of -$\underline{CH_2}$-OH disappeared completely and new signals ascribable to vinylidene protons of the methacryloyl group appeared at 5.54 and 6.11ppm. The functionality of methacryloyl group of the macromonomer was determined from the intensity ratio of the signals due to vinylidene protons and phenyl protons as 0.918. The values of the functionalities for PIB-OH and PIB macromonomer clearly indicate the complete conversion of -$CH_2OH$ group into -$CH_2$-O-CO-C($CH_3$)=$CH_2$ group.

*Anionic polymerization of PIB macromonomer*

The PIB macromonomer was polymerized by various anionic initiators including t-$C_4H_9MgBr$[9], t-$C_4H_9Li/(C_2H_5)_3Al$[10] and 1,1-diphenylhexyllithium (DPHLi)[11-14], which can afford living polymers of MMA under appropriate conditions. The results are shown in Table 1. The yield of polymacromonomer was calculated from the GPC trace of the reaction product. As a typical example the GPC curve for the reaction product from the polymerization of PIB macromonomer with DPHLi in THF at -78°C is shown in Figure 2. The yield was estimated as 95% from the areas under the peaks due to the poly-macromonomer formed and the unreacted starting macromonomer, correcting the functionality of the macromonomer (f=0.918). Polymerization with t-$C_4H_9MgBr$ in toluene at -60°C also gave polymacromonomer in high yield. Polymerization with n-$C_4H_9Li$ or t-$C_4H_9Li/(C_2H_5)_3Al$ gave rather lower yield than that with DPHLi or t-$C_4H_9MgBr$.

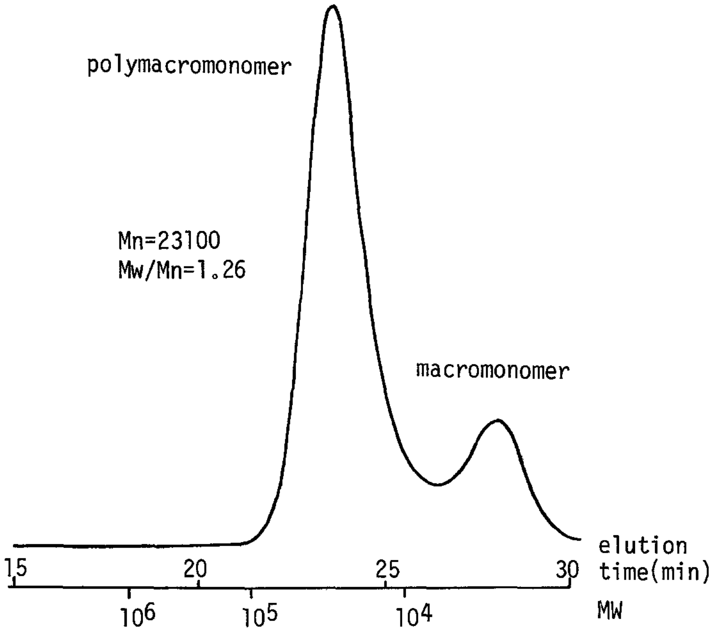


Figure 2 GPC curve of polymerization product prepared with 1,1-diphenylhexyllithium in THF at -78°C for 48hr.

The polymacromonomers was isolated from the reaction mixtures by repeated precipitation from toluene solution to methanol. The $^{13}C$ NMR spectrum of the polymacromonomer prepared with DPHLi in THF at -78°C is shown in Figure 3. The signals due to the polymethacrylate backbone of the polymacromonomer appear separately from the strong signals due to the PIB side chains. The signals of all sorts of carbons in the methacryloyl units show splittings due to the tacticity of the main chain as in the case of PMMA. The small signals due to initiator fragments, 1,1-diphenylhexyl group, are observed clearly at 14.1, 20.4, 21.5, 22.6 and 24.3ppm,

Table 1 Anionic Polymerization of PIB Macromonomer[a]

| Initiator | $[M]_0/[I]_0$ | Solv[b] | Temp. (°C) | Time (hr) | Conv[c] (%) | Mn VPO | Mn GPC | Mn Calcd | Mw[c]/Mn | Tacticity(%)[d] mm | mr | rr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $t-C_4H_9MgBr$ | 8.3 | Tol. | -60 | 168 | 91 | 26600 | 24800 | 17000 | 1.52 | 91 | 9 | 0 |
| $n-C_4H_9Li$ | 4.3 | Tol. | -78 | 72 | 56 | 30200 | 25600 | 5500 | 2.55 | 83 | 17 | 0 |
| $t-C_4H_9Li/(C_2H_5)_3Al$ | 8.8 | Tol. | -60 | 168 | 34 | 17300 | 14100 | 6700 | 1.32 | 5 | 43 | 52 |
| DPHLi[e] | 8.9 | THF | -78 | 48 | 95 | 22500 | 21300 | 19000 | 1.26 | 3 | 39 | 58 |
| DPHLi[e] | 8.0 | THF | -100 | 120 | 94 | 23200 | 19300 | 16900 | 1.20 | 2 | 36 | 62 |

[a] Macromonomer 0.20-0.22mmol, solvent 5 ml. [b] Tol. : toluene.
[c] Determined by GPC. [d] Determined from $^{13}C$ NMR signals of $\alpha$-$CH_3$ group.
[e] 1,1-Diphenylhexyllithium.

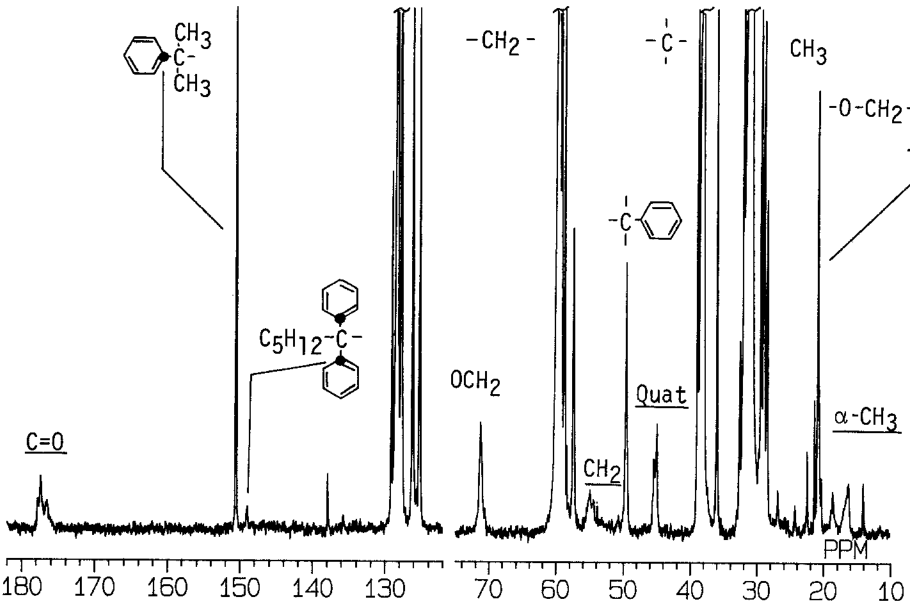


Figure 3 125MHz - C NMR spectrum of polymacromonomer prepared with 1,1-diphenylhexyllithium in THF at -78°C. Carbon species of methacryloyl units are underlined.

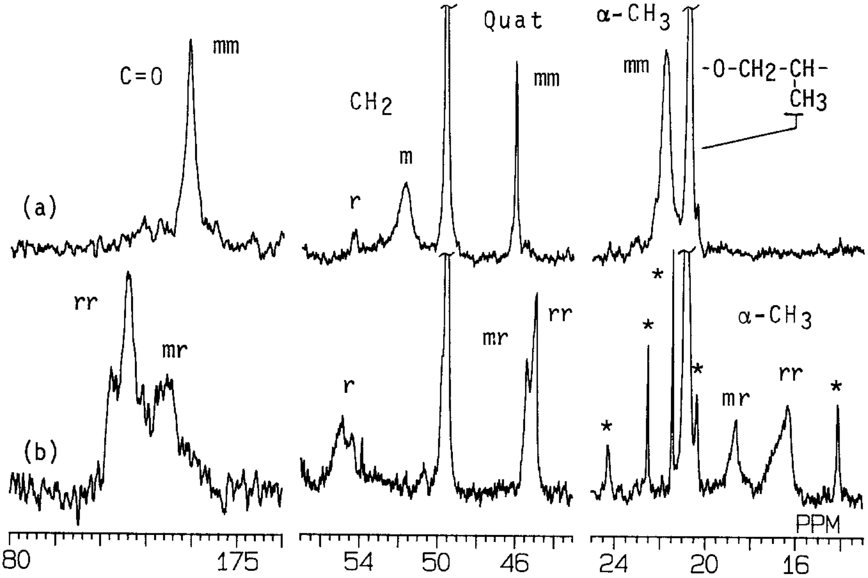


Figure 4 125MHz $^{13}$C NMR spectra of polymacromonomers prepared with t-$C_4H_9MgBr$ in toluene at -60°C (a) and 1,1-diphenylhexyllithium in THF at -78°C (b). Asterisked peaks are due to the initiator fragment.

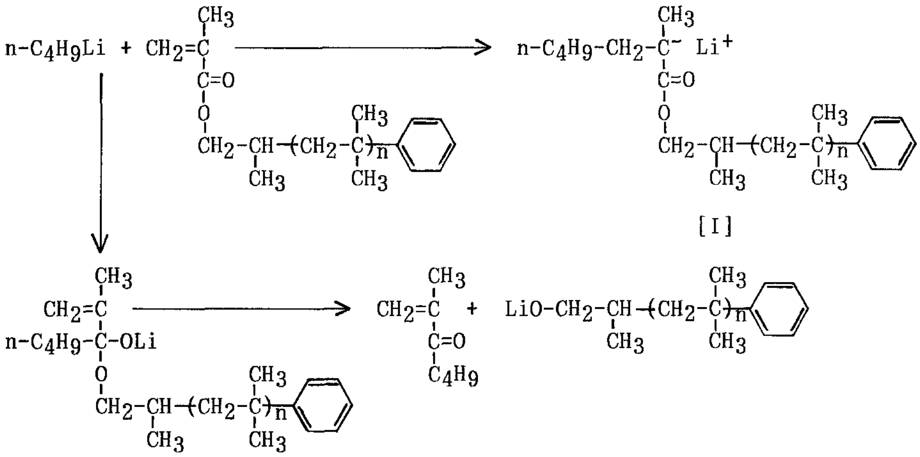
as seen in the expanded spectrum shown in Figure 4b. The degree of polymerization of the macromonomer was determined as 8.9 from the intensity ratio of the signals due to $CH_3$ group of the initiator fragment (at 14.1ppm) and $\alpha$-$CH_3$ group of methacryloyl unit. The value was in good agreement with the value expected from the amounts of the initiator charged and the macromonomer consumed. The molecular weight distribution observed by GPC was fairly narrow (Mw/Mn=1.26). These results suggest the living character of this polymerization.

Figure 4 shows the expanded spectra of the polymethacrylate backbone signal regions for the polymacromonomers prepared with t-$C_4H_9MgBr$ in toluene at -60°C and DPHLi in THF at -78°C. The signals of C=O, quaternary and $\alpha$-$CH_3$ carbons show the peak splittings due to triad tacticity and the signal of $CH_2$ carbon the splittings due to dyad tacticity. The peak assignments shown in Figure 4 were made by comparing the peak splittings with those observed in the spectrum of PMMA. Figure 4a clearly indicates that the polymacromonomer prepared with t-$C_4H_9MgBr$ is highly isotactic. As far as we are aware of, this is the first example of stereoregular polymerization of macromonomer. The polymacromonomer prepared with DPHLi in THF is syndiotactic-rich as in the case of PMMA formed under the same conditions.

The fractions of triad tacticity for the polymacromonomers prepared with various initiators were determined from the $\alpha$-$CH_3$ carbon signals and are shown in Table 1. The syndiotacticity of the polymacromonomer prepared with DPHLi in THF increased with decreasing polymerization temperature and the polymer formed at -100°C had 62% of triad syndiotacticity and Mw/Mn value of 1.20. Syndiotactic-rich polymacromonomer was also formed by t-$C_4H_9Li/(C_2H_5)_3Al$, which gives highly syndiotactic PMMA in toluene at low temperatures[10]. These syndiotactic-rich polymacromonomer has narrow MWD as shown in Table 1.

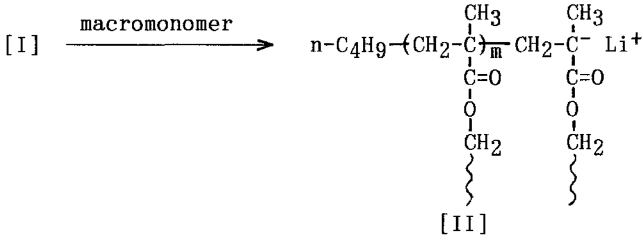
The mm triad of the polymacromonomer formed with t-$C_4H_9MgBr$ in toluene at -60°C was 91%. The MWD of this polymer was fairly narrow, though the Mn was a little larger than the calculated value. Further investigation is under way to examine the living character of this polymerization.

n-$C_4H_9Li$ also gave isotactic polymacromonomer but the MWD was much broader than those of the other polymacromonomers and the Mn was much larger than the calculated value. These results in the Mn and MWD are due to the side reaction of n-$C_4H_9Li$ with carbonyl group of methacryloyl unit of the macromonomer. The $^1H$ NMR spectrum of the lower molecular weight fraction of the polymerization product formed with n-$C_4H_9Li$ showed the signals due to the $CH_2$ group of PIB-OH observed at 3.4ppm along with those due to the unreacted PIB macromonomer. The PIB-OH should form along with butyl isopropenyl ketone through the reaction of n-$C_4H_9Li$ with the carbonyl group, as shown in equations (2)-(5). The butyl isopropenyl ketone is much more reactive than methacrylate monomer[15-18] so that it readily reacts with polymacromonomer anion [I] to form the less reactive anion [II]. Therefore, in the polymerization with n-$C_4H_9Li$, there exist at least two types of propagating anions which are very much different in reactivity. The lithium alkoxide of PIB-OH formed during the polymerization may coordinate with the propagating anions to change the reactivity and the stereoregularity. These are the reasons why the polymacromonomer prepared with n-$C_4H_9Li$ shows broader MWD and lower isotacticity. DPHLi and t-$C_4H_9MgBr$ are bulky enough not to be involved in the side reaction and gave the polymacromonomers with much narrower MWD. Suppression of such a side reaction is of primary importance for the control of the anionic polymerization of the macromonomer.

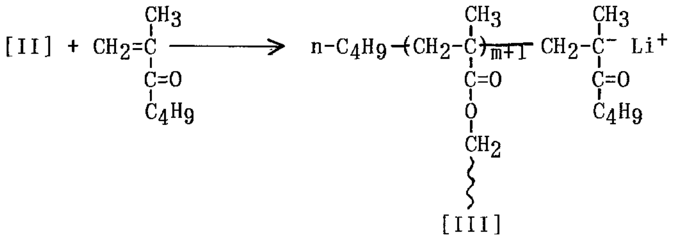


(2)

(3)



(4)



(5)

## Acknowledgements

The authors are grateful to Professor J. P. Kennedy of the University of Akron for his helpful discussion. A part of this work was supported by a Grant-in-Aid for Scientific Research (C) (No. 01550717) from the Ministry of Education, Science and Culture of Japan, and also by Kurata Foundation (1989-1990).

## Reference

1. Hatada K, Nakanishi H, Ute K, Kitayama T (1986) *Polym J* **18**: 581
2. Hatada K, Shinozaki T, Ute K, Kitayama T (1988) *Polym Bull* **19**: 231
3. Hatada K, Kitayama T, Ute K, Masuda E, Shionozaki T, Yamamoto M (1989) *Polym Bull* **21**: 165
4. Hatada K, Kitayama T, Masuda E, Kamachi M (1990) *Makromol Chem Rapid Commun* 11: 101
5. Hatada K, Kitayama T, Ute K (1989) *Prog Polym Sci* **13**: 189
6. Masson P, Franta E, Rempp P (1982) *Makromol Chem Rapid Commun* **3**: 499
7. Asami R, Kyuda K, Takaki M, Ogawa Y (1982) *Polym Prepr Jpn* **31**: 277
8. Kennedy J P, Hiza M (1983) *Polym Bull* **10**: 146
9. Hatada K, Ute K, Tanaka K, Okamoto Y, Kitayama T (1986) *Polym J* **18**: 1037
10. Kitayama T, Shinozaki T, Sakamoto T, Yamamoto M, Hatada K (1989) *Makromol Chem Supplement* **15**: 167
11. Anderson B C, Amdrews G D, Arthur Jr P, Jacobson H W, Playtis A J, Sharkey W H (1981) *Macromolecules* **14**: 1599
12. Das R K, Allen R D, Ward T C, McGrath J E, Dodson R J (1984) *Polym Prep Am Chem Soc; Div Polym Chem* **25(1)**: 185
13. Lutz P, Masson P, Beinert G, Rempp P (1984) *Polym. Bull.*, **12**: 79
14. Cao Z-K, Okamoto Y, Hatada K (1986) *Kobunshi Ronbunshu* **43**: 857
15. Hatada K, Kitayama T, Fujikawa K, Ohta K, Yuki H (1981) *Anionic Polymerization; Kinetics, Mechanism, and Synthesis(J.E. McGrath Ed.), ACS Symposium Series* **166**: 327
16. Hatada K, Kitayama T, Okahata S, Yuki H (1981) *Polym J* **13**: 1045
17. Hatada K, Kitayama T, Okahata S, Yuki H (1982) *Polym J* **14**: 971
18. Ute K, Kitayama T, Hatada K (1986) *Polym J* **18**: 249

Accepted November 12, 1990 S